

24 January 2002

## HAIR CONDITIONING COMPOSITION COMPRISING HYDROPHOBICALLY MODIFIED CELLULOSE ETHER

### TECHNICAL FIELD

The present invention relates to hair conditioning composition comprising a hydrophobically modified cellulose ether.

### BACKGROUND

Human hair becomes soiled due to its contact with the surrounding environment and from the sebum secreted by the scalp. The soiling of hair causes it to have a dirty feel and an unattractive appearance. The soiling of the hair necessitates shampooing with frequent regularity.

Shampooing cleans the hair by removing excess soil and sebum. However, shampooing can leave the hair in a wet, tangled, and generally unmanageable state. Once the hair dries, it is often left in a dry, rough, lusterless, or frizzy condition due to removal of the hair's natural oils and other natural conditioning and moisturizing components. The hair can further be left with increased levels of static upon drying, which can interfere with combing and result in a condition commonly referred to as "fly-away hair", or contribute to an undesirable phenomena of "split ends", particularly for long hair.

A variety of approaches have been developed to alleviate these after-shampoo problems. These approaches range from post-shampoo application of hair conditioners such as leave-on and rinse-off products, to hair conditioning shampoos which attempt to both clean and condition the hair from a single product.

Although some consumers prefer the ease and convenience of a shampoo which includes conditioners, a substantial proportion of consumers prefer the more conventional conditioner formulations which are applied to the hair as a separate step from shampooing, usually subsequent to shampooing.

Conditioning formulations can be in the form of rinse-off products or leave-on products, and can be in the form of an emulsion, cream, gel, spray, and mousse. Such consumers who prefer the conventional conditioner formulations value the relatively higher conditioning effect, or convenience of changing the amount of conditioning depending on the condition of hair or amount of hair.

Some consumers with fine hair have a desire to volume-up their hair. The term "hair volume-up" as used herein is not equal to fly-away hair. Fly-away hair is due to the increased level of static, and represents volume increase of only very minor amount of the hair as a whole, and is not desirable. On the other hand, hair volume-up as used herein relates to increase of the bulk of the hair volume. Consumers having fine hair have the desire to achieve hair volume-up while controlling undesirable fly-away of the hair. Generally, hair conditioner products targeted for such consumers provided the volume-up or less volume-down benefit by decreasing the level of conditioning actives included in the composition. This is thought to be emerging from the concept that conditioning actives weigh down the hair. Consequently, hair conditioner products targeted for consumers which desire volume-up generally had only compromised conditioning benefits.

Based on the foregoing, there remains a desire to provide hair conditioning compositions which provide hair volume-up while not compromising basic conditioning benefits such as soft, smooth, easy to comb, clean, draggy feel to the hair.

United States Patents 5,100,658, 5,106,609, and 5,855,878 disclose the use of hydrophobically modified nonionic water-soluble polymers in hair conditioning compositions. It is disclosed in each reference that such composition provides effective delivery of an active cosmetic component to the hair or skin. European Patent Application EP-0,875,557-A discloses aqueous compositions of surfactant mixtures with hydrophobically-modified polymers; in particular, hydrophobically-modified polymeric rheology modifiers (thickeners) to provide enhanced thickening efficiency. European Patent Application EP-0,786,249-A discloses a topical composition containing active cosmetic and/or dermatological agent including cetyl hydroxyethyl cellulose as gelling agent.

Hair conditioning compositions containing hydrophobically modified cellulose polymers can become very viscous and provide negative performance to the feel of hair or manufacturing of the composition. Thus, there is also a

desire to provide such hair conditioning compositions while maintaining acceptable rheology profiles to provide satisfactory spreadability on the hair, and so as to be made by a convenient manufacturing method.

None of the existing art provides all of the advantages and benefits of the present invention.

### SUMMARY

The present invention is directed to a hair conditioning composition comprising by weight:

- (a) from about 0.001% to about 2% of a hydrophobically modified cellulose ether comprising a hydrophilic cellulose backbone and a hydrophobic substitution group; the hydrophilic cellulose backbone being water soluble and selected from the group consisting of methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxyethyl ethylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, hydroxybutyl cellulose, and mixtures thereof; and having grafted thereto the hydrophobic substitution group to render the hydrophobically modified cellulose ether to have less than 1% water solubility, the hydrophobic substitution group selected from a straight or branched chain alkyl group of from about 10 to about 22 carbons; wherein the ratio of the hydrophilic groups in the hydrophilic cellulose backbone to the hydrophobic substitution group being from about 2:1 to about 1000:1;
- (b) from about 0.1% to about 15% of a high melting point fatty compound having a melting point of 25°C or higher;
- (c) from about 0.1% to about 10% of a cationic conditioning agent having saturated alkyl groups; and
- (d) an aqueous carrier.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

### DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

#### HYDROPHOBICALLY MODIFIED CELLULOSE ETHER

The composition of the present invention comprises by weight from about 0.001% to about 2%, preferably from about 0.01% to about 0.5%, more preferably from about 0.05% to about 0.5%, of a hydrophobically modified cellulose ether.

The hydrophobically modified cellulose ethers useful herein have been known in the art as hydrophilic thickeners to aqueous compositions. It has been surprisingly found that, when included in a gel matrix vehicle system at certain levels, the hydrophobically modified cellulose ethers provide increase in bulk hair volume. It has further been surprisingly found that cellulose ethers with no hydrophobic modifications, such as hydroxyethyl cellulose, do not provide such increase in bulk hair volume. Without being bound by theory, it is believed this is due to the significant substantivity and controlled water solubility of the hydrophobically modified cellulose ethers herein. The hydrophobically modified cellulose ethers would deposit on the hair as discrete particles, thus enhance the inter fiber interactions and change its spatial orientation, and consequently provide more volume to the hair.

The controlled level of hydrophobically modified cellulose ether also provides acceptable rheology profiles in the conditioning composition of this invention, so this composition provides satisfactory spreadability on the hair, and can be made by a convenient manufacturing method.

The hydrophobically modified cellulose ethers useful herein comprise a hydrophilic cellulose backbone and a hydrophobic substitution group. The hydrophilic cellulose backbone has a sufficient degree of nonionic substitution to

cellulose to be water soluble. Such hydrophilic cellulose backbone is selected from the group consisting of methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxyethyl ethylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, hydroxybutyl cellulose, and mixtures thereof. The amount of nonionic substitution is not critical, so long as there is an amount sufficient to assure that the hydrophilic cellulose backbone is water soluble. The hydrophilic cellulose backbone has a molecular weight of about less than 800,000, preferably from about 20,000 to about 700,000, or from about 75 D. P. to about 2500 D. P. Further, where a high viscosity building effect is not desirable, a lower molecular weight cellulose backbone is preferred. One of the preferred hydrophilic cellulose backbone is hydroxyethyl cellulose having a molecular weight of from about 50,000 to about 700,000. Hydroxyethyl cellulose of this molecular weight is known to be one of the most hydrophilic of the materials contemplated. Thus, hydroxyethyl cellulose can be modified to a greater extent than other hydrophilic cellulose backbones.

The hydrophilic cellulose backbone is further substituted with a hydrophobic substitution group via an ether linkage to render the hydrophobically modified cellulose ether to have less than 1% water solubility, preferably less than 0.2% water solubility. The hydrophobic substitution group is selected from a straight or branched chain alkyl group of from about 10 to about 22 carbons; wherein the ratio of the hydrophilic groups in the hydrophilic cellulose backbone to the hydrophobic substitution group being from about 2:1 to about 1000:1, preferably from about 10:1 to about 100:1.

Commercially available hydrophobically modified cellulose ethers useful herein include: cetyl hydroxyethylcellulose having tradenames NATROSOL PLUS 330CS and POLYSURF 67, both available from Aqualon Company, Del, USA, having cetyl group substitution of about 0.4% to about 0.65% by weight of the entire polymer.

#### HIGH MELTING POINT FATTY COMPOUND

The composition of the present invention comprises a high melting point fatty compound. The high melting point fatty compound useful herein have a melting point of 25°C or higher, and is selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one

classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

These high melting point fatty compounds, together with the cationic conditioning agent, provide a gel network suitable for providing various conditioning benefits such as slippery and slick feel on wet hair, and softness, moisturized feel, and fly-away control on dry hair.

The high melting point fatty compound is included in the composition at a level by weight of from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 7%.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols are saturated and can be straight or branched chain alcohols. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids are saturated and can be straight or branched chain acids. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid

derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, *i.e.* a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C<sub>1</sub>-C<sub>30</sub> alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

High melting point fatty compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point fatty compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from Shin Nihon Rika (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy).

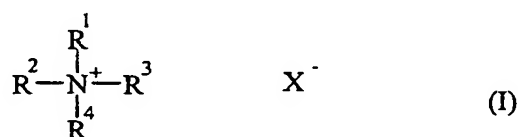
#### CATIONIC CONDITIONING AGENT

The composition of the present invention comprises a cationic conditioning agent. This cationic conditioning agent, together with the high melting point fatty compounds, provide a gel network suitable for providing various conditioning benefits such as slippery and slick feel on wet hair, and such as softness, moisturized feel, and fly-away control on dry hair.

The cationic conditioning agent is included in the composition at a level by weight of from about 0.1% to about 10%, preferably from about 0.25% to about 8%, more preferably from about 0.5% to about 3%.

The cationic conditioning agent herein is selected from cationic surfactants having saturated alkyl groups. Cationic surfactants having unsaturated alkyl groups provide a suitable gel network and provides good hair feel.

The cationic surfactants useful herein include those corresponding to the general formula (I):

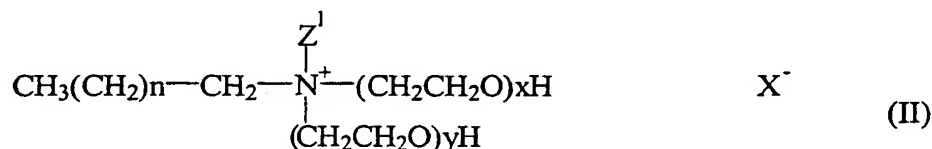


wherein at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, are saturated. Preferred is when R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently selected from C<sub>1</sub> to about C<sub>22</sub> alkyl. Nonlimiting examples of cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-14, quaternium-18, quaternium-18 methosulfate, quaternium-24, and mixtures thereof.

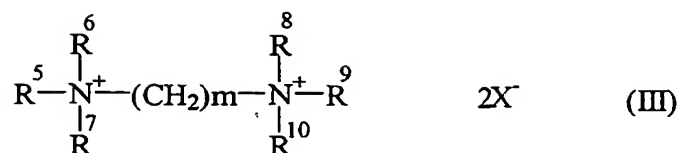


Among the cationic surfactants of general formula (I), preferred are those containing in the molecule at least one alkyl chain having at least 16 carbons. Nonlimiting examples of such preferred cationic surfactants include: behenyl trimethyl ammonium chloride available, for example, with tradename INCROQUAT TMC-80 from Croda and ECONOL TM22 from Sanyo Kasei; cetyl trimethyl ammonium chloride available, for example, with tradename CA-2350 from Nikko Chemicals, hydrogenated tallow alkyl trimethyl ammonium chloride, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, di(behenyl/arachidyl) dimethyl ammonium chloride, dibehenyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl propyleneglycol phosphate dimethyl ammonium chloride, stearyl amidopropyl dimethyl benzyl ammonium chloride, stearyl amidopropyl dimethyl (myristylacetate) ammonium chloride, and N-(stearyl colamino formyl methy) pyridinium chloride.

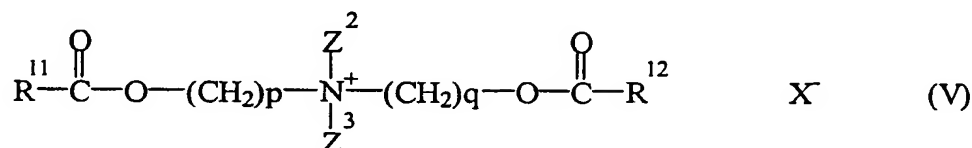
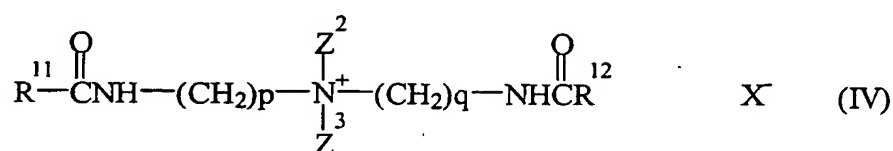
Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R<sup>1</sup> - R<sup>4</sup> radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C<sub>1</sub> - C<sub>3</sub> alkoxy), polyoxyalkylene (preferably C<sub>1</sub> - C<sub>3</sub> polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VIII) below:



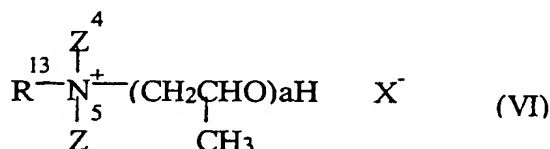
wherein n is from 8 to about 28, x+y is from 2 to about 40, Z<sup>1</sup> is a short chain alkyl, preferably a C<sub>1</sub> - C<sub>3</sub> alkyl, more preferably methyl, or (CH<sub>2</sub>CH<sub>2</sub>O)<sub>z</sub>H wherein x+y+z is up to 60, and X is a salt forming anion as defined above;



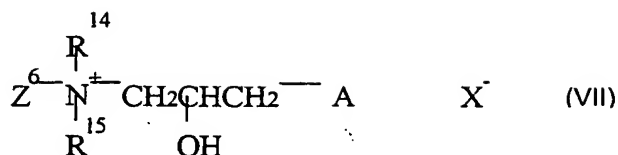
wherein m is 1 to 5, one or more of R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently an C<sub>1</sub> - C<sub>30</sub> alkyl, the remainder are CH<sub>2</sub>CH<sub>2</sub>OH, one or two of R<sup>8</sup>, R<sup>9</sup>, and R<sup>10</sup> are independently an C<sub>1</sub> - C<sub>30</sub> alkyl, and remainder are CH<sub>2</sub>CH<sub>2</sub>OH, and X is a salt forming anion as mentioned above;



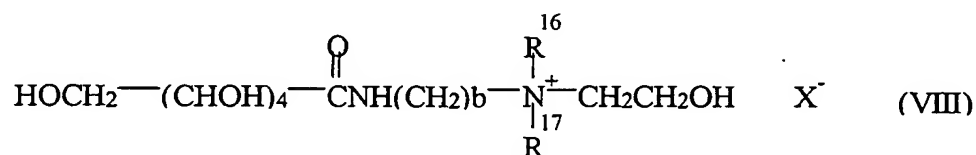
wherein, independently for formulae (IV) and (V), Z<sup>2</sup> is an alkyl, preferably a C<sub>1</sub> - C<sub>3</sub> alkyl, more preferably methyl, and Z<sup>3</sup> is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, p and q independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2, R<sup>11</sup> and R<sup>12</sup>, independently, are substituted or unsubstituted hydrocarbyls, preferably C<sub>12</sub> - C<sub>20</sub> alkyl, and X is a salt forming anion as defined above;



wherein R<sup>13</sup> is a hydrocarbyl, preferably a C<sub>1</sub> - C<sub>3</sub> alkyl, more preferably methyl, Z<sup>4</sup> and Z<sup>5</sup> are, independently, short chain hydrocarbyls, preferably C<sub>2</sub> - C<sub>4</sub> alkyl, more preferably ethyl, a is from 2 to about 40, preferably from about 7 to about 30, and X is a salt forming anion as defined above;



wherein R<sup>14</sup> and R<sup>15</sup>, independently, are C<sub>1</sub> - C<sub>3</sub> alkyl, preferably methyl, Z<sup>6</sup> is a C<sub>12</sub> - C<sub>22</sub> hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and X is a salt forming anion as defined above;



wherein b is 2 or 3, R<sup>16</sup> and R<sup>17</sup>, independently are C<sub>1</sub> - C<sub>3</sub> hydrocarbyls preferably methyl, and X is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-61, quaternium-62, quaternium-70, quaternium-71, quaternium-75, quaternium-76 hydrolyzed collagen, quaternium-77, quaternium-78, quaternium-80, quaternium-83, and mixtures thereof.

Highly preferred hydrophilically substituted cationic surfactants include dialkylamido ethyl hydroxyethylmonium salt, dialkylamidoethyl dimonium salt, dialkylol ethyl hydroxyethylmonium salt, dialkylol ethyldimonium salt, and mixtures thereof; for example, commercially available under the following tradenames; VARISOFT 110, VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from about

12 to about 22 carbon atoms, and can be substituted or unsubstituted. Particularly useful are amidoamines of the following general formula:



wherein  $R^1$  is a residue of  $C_{11}$  to  $C_{24}$  fatty acids,  $R^2$  is a  $C_1$  to  $C_4$  alkyl,

5 and  $m$  is an integer from 1 to 4.

Preferred amidoamine useful in the present invention includes  
 stearamidopropyl dimethylamine, stearamidopropyl diethylamine,  
 stearamidoethyl diethylamine, stearamidoethyl dimethylamine,  
 palmitamidopropyl dimethylamine, palmitamidopropyl diethylamine,  
 10 palmitamidoethyl diethylamine, palmitamidoethyl dimethylamine,  
 behenamidopropyl dimethylamine, behenamidopropyl diethylamine,  
 behenamidoethyl diethylamine, behenamidoethyl dimethylamine,  
 arachidamidopropyl dimethylamine, arachidamidopropyl diethylamine,  
 arachidamidoethyl diethylamine, arachidamidoethyl dimethylamine, and mixtures  
 15 thereof; more preferably stearamidopropyl dimethylamine,  
 stearamidoethyl diethylamine, and mixtures thereof.

The amidoamines herein are preferably partially quaternized with the acids selected from the group consisting of L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, L-glutamic acid hydrochloride, tartaric acid, and mixtures thereof; preferably L-glutamic acid,  
 20 lactic acid, hydrochloric acid, and mixtures thereof.

Preferably, the mole ratio of amidoamine to acid is from about 1:0.3 to about 1:1, more preferably from about 1:0.5 to about 1:0.9.

#### AQUEOUS CARRIER

25 The composition of the present invention comprises an aqueous carrier. The level and species of the carrier are selected according to the compatibility with other components, and other desired characteristic of the product.

The carrier useful in the present invention include water and water solutions of lower alkyl alcohols and polyhydric alcohols. The lower alkyl alcohol useful herein are monohydric alcohols having 1 to 6 carbons, more preferably  
 30 ethanol and isopropanol. The polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, and propane diol.

Preferably, the aqueous carrier is substantially water. Deionized water is preferably used. Water from natural sources including mineral cations can also  
 35 be used, depending on the desired characteristic of the product. Generally, the

compositions of the present invention comprise from about 20% to about 95% , preferably from about 30% to about 92%, and more preferably from about 50% to about 90% water.

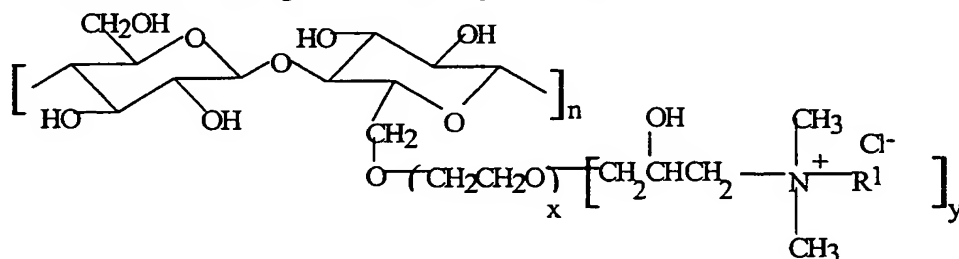
### CATIONIC POLYMER

The hair conditioning composition of the present invention may further comprise a cationic polymer selected from the group consisting of hydrophobically modified cationic cellulose, a copolymer of hydrophilic-cellulose and diallyldimethyl ammonium chloride, and mixtures thereof.

The cationic polymers herein provide increase in bulk hair volume while not deteriorating conditioning benefits such as fly-away control. The cationic polymers herein are typically included in the hair styling compositions as an antistatic agent, a film former, or a hair fixative. It has been surprisingly found that, when the cationic polymers are included in hair conditioning compositions in combination with the hydrophobically modified cellulose ether, increase in bulk hair volume is improved, and increased draggy and clean feel to the hair is provided.

The hair conditioning composition of the present invention may comprise by weight from about 0.001% to about 5%, preferably from about 0.05% to about 2.0%, more preferably from about 0.1% to about 1.0% of a cationic polymer.

The hydrophobically modified cationic celluloses useful in the present invention are those having the following formula:



wherein  $R^1$  is an alkyl having from about 8 to about 22 carbons, preferably from about 10 to about 18 carbons;  $n$  is an integer from 1 to about 10,000, preferably from about 100 to about 4,000;  $x$  is 0 or an integer from 1 to about 6, preferably from about 1 to about 3; and  $y$  is the level of cationic substitution from 0.1 to 1.0.

Commercially available hydrophobically modified cationic celluloses include, for example, the polymeric quaternary ammonium salts of hydroxyethyl

cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24, available from Amerchol Corp. (Edison, NJ, USA) under the tradenames Polymer LM-200® and BioCare Polymer HA-24.

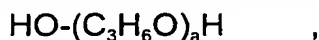
5        The copolymers of hydrophilic-cellulose and diallyldimethyl ammonium chloride useful herein are those having hydrophilic-cellulose units and diallyldimethyl ammonium chloride units, the hydrophilic cellulose units selected from the group consisting of methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxyethyl ethylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, hydroxybutyl cellulose, and mixtures thereof, preferably hydroxyethylcellulose. The ratio of the number of the hydrophilic-cellulose units to the diallyldimethyl ammonium chloride units comprised in the copolymer is from about 1:100 to about 10:1, preferably from about 1:10 to about 10:1, more preferably from about 1:3 to about 5:1, still preferably from about 1:1 to about 3:1, and wherein the molecular weight of the copolymer is from about 10,000 to about 250,000, preferably from about 15,000 to about 200,000. To provide preferred copolymers, the hydrophilic-cellulose units are contained at a range of from about 40 to about 350, and the diallyldimethyl ammonium chloride units are contained at a range of from about 40 to about 120.

20        Highly suitable copolymers are hydroxyethylcellulose diallyldimethyl ammonium chloride copolymers known in the industry as Polyquaternium-4 (CTFA Dictionary). Commercially available hydroxyethylcellulose diallyldimethyl ammonium chloride copolymers are those with tradenames CELQUAT L-200 and CELQUAT H-100 available from National Starch Corp.

#### 25        POLYPROPYLENE GLYCOL

30        The hair conditioning composition of the present invention may further comprise a polypropylene glycol. The polypropylene glycol useful herein is selected from single-polypropylene glycol-chain segment polymers, multi-polypropylene glycol-chain segment polymers, and mixtures thereof, having a weight average molecular weight of from about 200 g/mol to about 100,000 g/mol, preferably from about 1,000 g/mol to about 60,000 g/mol. When included in the composition of the present invention in combination with the hydrophobically modified cellulose ether, polypropylene glycol may deliver flyaway hair control benefits without affecting the bulk hair volume.

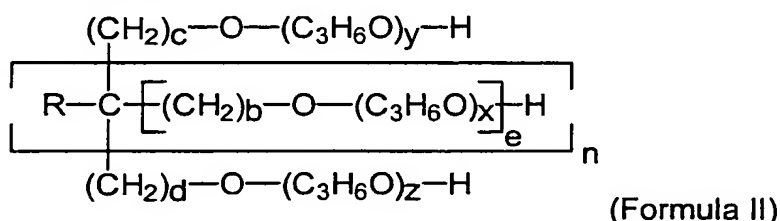
Accordingly, a highly preferred single-polypropylene glycol-chain segment polymer has the following formula:



wherein a is a value from about 4 to about 400, preferably from about 20 to about 100, and more preferably from about 20 to about 40.

The single-polypropylene glycol-chain segment polymer useful herein is typically inexpensive, and is readily available from, for example, Sanyo Kasei (Osaka, Japan), Dow Chemicals (Midland, Michigan, USA), Calgon Chemical, Inc. (Skokie, Illinois, USA), Arco Chemical Co. (Newton Square Pennsylvania, USA), Witco Chemicals Corp. (Greenwich, Connecticut, USA), and PPG Specialty Chemicals (Gurnee, Illinois, USA).

A highly preferred multi-polypropylene glycol-chain segment polymer has the following formula:



wherein n is a value from about 0 to about 10, preferably from about 0 to about 7, and more preferably from about 1 to about 4. In Formula II, each R is independently selected from the group consisting of H, and C<sub>1</sub>-C<sub>30</sub> alkyl, and preferably each R is independently selected from the group consisting of H, and C<sub>1</sub>-C<sub>4</sub> alkyl. In Formula II, each b is independently a value from about 0 to about 2, preferably from about 0 to about 1, and more preferably b = 0. Similarly, c and d are independently a value from about 0 to about 2, preferably from about 0 to about 1. However, the total of b + c + d is at least about 2, preferably the total of b + c + d is from about 2 to about 3. Each e is independently a value of 0 or 1, if n is from about 1 to about 4, then e is preferably equal to 1. Also in Formula II, x, y, and z are independently a value of from about 1 to about 120, preferably from about 7 to about 100, and more preferably from about 7 to about 100, where x + y + z is greater than about 20.

Examples of the multi-polypropylene glycol-chain segment polymer of Formula II which is especially useful herein includes polyoxypropylene glyceryl ether (n = 1, R = H, b = 0, c and d = 1, e = 1, and x, y, and z independently indicate the degree of polymerization of their respective polypropylene glycol-

chain segments; available as New Pol GP-4000, from Sanyo Kasei of Osaka, Japan), polypropylene trimethylol propane ( $n = 1$ ,  $R = C_2H_5$ ,  $b = 1$ ,  $c$  and  $d = 1$ ,  $e = 1$ , and  $x$ ,  $y$ , and  $z$  independently indicate the degree of polymerization of their respective polypropylene glycol-chain segments), polyoxypropylene sorbitol ( $n = 4$ , each  $R = H$ ,  $b = 0$ ,  $c$  and  $d = 1$ , each  $e = 1$ , and  $y$ ,  $z$ , and each  $x$  independently indicate the degree of polymerization of their respective polypropylene glycol-chain segments; available as New Pol SP-4000, from Sanyo Kasei, Osaka, Japan), and PPG-10 butanediol ( $n = 0$ ,  $c$  and  $d = 2$ , and  $y + z = 10$ ; available as Probutyl DB-10, from Croda, Inc., of Parsippany, New Jersey, U.S.A.).

#### RHEOLOGY MODIFIER

The hair conditioning composition of the present invention may further comprise a rheology modifier. The rheology modifier may be any polymer which increases the rheology of the composition, and which are compatible with the other polymers included in the composition, and do not negatively affect the benefits provided by the composition. Rheology modifiers particularly suitable in the present invention are those selected from the group consisting of methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxyethyl ethylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose, hydroxybutyl cellulose, and mixtures thereof. Without being bound by theory, it is believed that, by the rheology being increased, the composition provides better spreadability to the hair and increases deposition of components such as the hydrophobically modified cellulose ether and the cationic polymer to the hair. Commercially available hydroxyethyl ethylcellulose are those available from Akzo Nobel with tradename Elfacos CD481.

#### LOW MELTING POINT OIL

The hair conditioning composition of the present invention may further comprise a low melting point oil, which has a melting point of less than  $25^{\circ}C$ , and is preferably included in the composition at a level by weight of from about 0.1% to about 10%, more preferably from about 0.25% to about 6%.

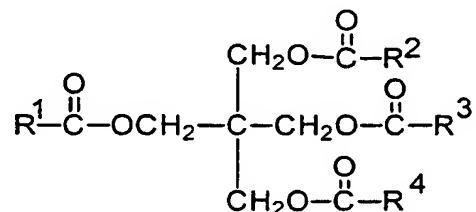
Low melting point oils useful herein include unsaturated fatty alcohols having from about 10 to about 30 carbon atoms, unsaturated fatty acids having from about 10 to about 30 carbon atoms, fatty acid derivatives, fatty alcohol derivatives, ester oils, and mixtures thereof. Fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon



atoms. These fatty alcohols are unsaturated and can be straight or branched chain alcohols. Suitable fatty alcohols include, for example, oleyl alcohol, isostearyl alcohol, tridecylalcohol, decyl tetradecyl alcohol, and octyl dodecyl alcohol. These alcohols are available, for example, from Shinnihon Rika.

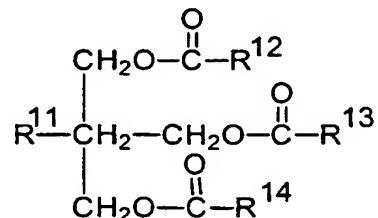
Low melting point oils useful herein include pentaerythritol ester oils, trimethylol ester oils, poly  $\alpha$ -olefin oils, citrate ester oils, glyceryl ester oils, and mixtures thereof, and the ester oil useful herein is water-insoluble. As used herein, the term "water-insoluble" means the compound is substantially not soluble in water at 25°C; when the compound is mixed with water at a concentration by weight of above 1.0%, preferably at above 0.5%, the compound is temporarily dispersed to form an unstable colloid in water, then is quickly separated from water into two phases.

Pentaerythritol ester oils useful herein are those having the following formula:



wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$ , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$ , independently, are branched, straight, saturated, or unsaturated alkyl groups having from about 8 to about 22 carbons. More preferably,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are defined so that the molecular weight of the compound is from about 800 to about 1200.

Trimethylol ester oils useful herein are those having the following formula:



wherein  $\text{R}^{11}$  is an alkyl group having from 1 to about 30 carbons, and  $\text{R}^{12}$ ,  $\text{R}^{13}$ , and  $\text{R}^{14}$ , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably,

R<sup>11</sup> is ethyl and R<sup>12</sup>, R<sup>13</sup>, and R<sup>14</sup>, independently, are branched, straight, saturated, or unsaturated alkyl groups having from 8 to about 22 carbons. More preferably, R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>14</sup> are defined so that the molecular weight of the compound is from about 800 to about 1200.

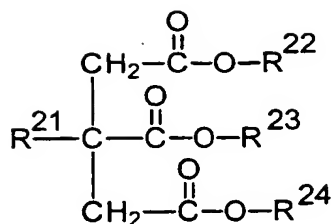
5 Particularly useful pentaerythritol ester oils and trimethylol ester oils herein include pentaerythritol tetraisostearate, pentaerythritol tetraoleate, trimethylolpropane triisostearate, trimethylolpropane trioleate, and mixtures thereof. Such compounds are available from Kokyo Alcohol with tradenames KAKPTI, KAKTTI, and Shin-nihon Rika with tradenames PTO, ENUJERUBU  
10 TP3SO.

Poly  $\alpha$ -olefin oils useful herein are those derived from 1-alkene monomers having from about 6 to about 16 carbons, preferably from about 6 to about 12 carbons atoms. Nonlimiting examples of 1-alkene monomers useful for preparing the poly  $\alpha$ -olefin oils include 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, branched isomers such as 4-methyl-1-pentene, and mixtures thereof. Preferred 1-alkene monomers useful for preparing the poly  $\alpha$ -olefin oils are 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and mixtures thereof. Poly  $\alpha$ -olefin oils useful herein further have a viscosity of from about 1 to about 35,000 cst, a molecular  
15 weight of from about 200 to about 60,000, and a polydispersity of no more than about 3.

Poly  $\alpha$ -olefin oils having a molecular weight of at least about 800 are useful herein. Such high molecular weight poly  $\alpha$ -olefin oils are believed to provide long lasting moisturized feel to the hair. Poly  $\alpha$ -olefin oils having a  
25 molecular weight of less than about 800 are useful herein. Such low molecular weight poly  $\alpha$ -olefin oils are believed to provide a smooth, light, clean feel to the hair.

Particularly useful poly  $\alpha$ -olefin oils herein include polydecenes with tradenames PURESYN 6 having a number average molecular weight of about  
30 500 and PURESYN 100 having a number average molecular weight of about 3000 and PURESYN 300 having a number average molecular weight of about 6000 available from Mobil Chemical Co.

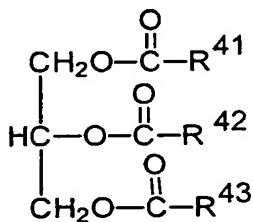
Citrate ester oils useful herein are those having a molecular weight of at least about 500 having the following formula:



wherein  $\text{R}^{21}$  is OH or  $\text{CH}_3\text{COO}$ , and  $\text{R}^{22}$ ,  $\text{R}^{23}$ , and  $\text{R}^{24}$ , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably,  $\text{R}^{21}$  is OH, and  $\text{R}^{22}$ ,  $\text{R}^{23}$ , and  $\text{R}^{24}$ , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably,  $\text{R}^{21}$ ,  $\text{R}^{22}$ ,  $\text{R}^{23}$  and  $\text{R}^{24}$  are defined so that the molecular weight of the compound is at least about 800.

Particularly useful citrate ester oils herein include triisocetyl citrate with tradename CITMOL 316 available from Bernel, triisostearyl citrate with tradename PELEMOL TISC available from Phoenix, and trioctyldodecyl citrate with tradename CITMOL 320 available from Bernel.

Glyceryl ester oils useful herein are those having a molecular weight of at least about 500 and having the following formula:



wherein  $\text{R}^{41}$ ,  $\text{R}^{42}$ , and  $\text{R}^{43}$ , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably,  $\text{R}^{41}$ ,  $\text{R}^{42}$ , and  $\text{R}^{43}$ , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably,  $\text{R}^{41}$ ,  $\text{R}^{42}$ , and  $\text{R}^{43}$  are defined so that the molecular weight of the compound is at least about 800.

Particularly useful glyceryl ester oils herein include triisostearin with tradename SUN ESPOL G-318 available from Taiyo Kagaku, triolein with tradename CITHROL GTO available from Croda Surfactants Ltd., trilinolein with tradename EFADERMA-F available from Vevy, or tradename EFA-GLYCERIDES from Brooks.

### POLYETHYLENE GLYCOL

The composition of present invention may further comprise a polyethylene glycol having the formula:



5 wherein n has an average value of from about 2,000 to about 14,000, preferably from about 5,000 to about 9,000, more preferably from about 6,000 to about 8,000.

The polyethylene glycol is preferably included in the composition at a level by weight of from about 0.1% to about 10%, more preferably from about 0.25%  
10 to about 6%.

The polyethylene glycol described above is also known as a polyethylene oxide, or polyoxyethylene. Polyethylene glycols useful herein that are especially preferred are PEG-2M wherein n has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10 from Union Carbide and as PEG-2,000);  
15 PEG-5M wherein n has an average value of about 5,000 (PEG-5M is also known as Polyox WSR® N-35 and as Polyox WSR® N-80, both from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein n has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 from Union Carbide); PEG-9M wherein n has an average value of about 9,000  
20 (PEG-9M is also known as Polyox WSR® N-3333 from Union Carbide); and PEG-14M wherein n has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 from Union Carbide).

### SILICONE COMPOUND

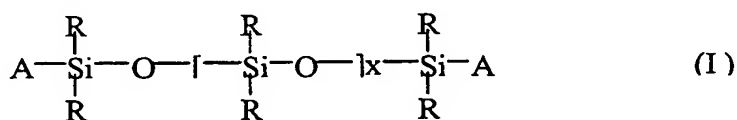
The present composition may further contain a silicone compound. The  
25 amount of silicone compound to the entire composition is preferably from about 0.1% to about 10% by weight. The silicone compounds hereof can include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase.  
30 By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The silicone compounds herein may be made by conventional polymerization, or emulsion polymerization.

The silicone compounds for use herein will preferably have a viscosity of  
35 from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from

about 10,000 to about 1,800,000, and even more preferably from about 25,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970, which is incorporated by reference herein in its entirety. Silicone compound of high molecular weight may be made by emulsion polymerization.

Silicone compounds useful herein include polyalkyl polyaryl siloxanes, polyalkyleneoxide-modified siloxanes, silicone resins, amino-substituted siloxanes, and mixtures thereof. The silicone compound is preferably selected from the group consisting of polyalkyl polyaryl siloxanes, polyalkyleneoxide-modified siloxanes, silicone resins, and mixtures thereof, and more preferably from one or more polyalkyl polyaryl siloxanes.

Polyalkyl polyaryl siloxanes useful here in include those with the following structure (I)



wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

Polymethylphenylsiloxanes, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid, are useful herein.

Also preferred, for enhancing the shine characteristics of hair, are highly  
5 arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the  
10 material.

Another polyalkyl polyaryl siloxane that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein  
15 can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are  
20 General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane,  
25 poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Polyalkyleneoxide-modified siloxanes useful herein include, for example, polypropylene oxide modified and polyethylene oxide modified polydimethylsiloxane. The ethylene oxide and polypropylene oxide level should  
30 be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Silicone resins, which are highly crosslinked polymeric siloxane systems, are useful herein. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or  
35 both, silanes during manufacture of the silicone resin. As is well understood in

the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

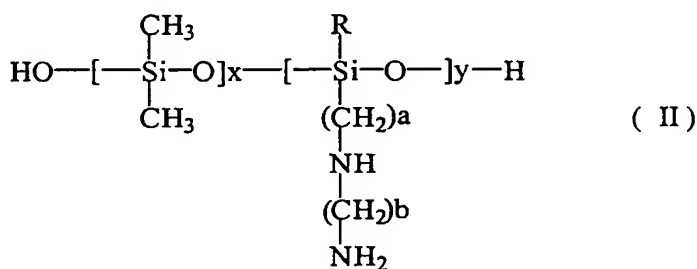
Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl<sup>TM</sup> from Toshiba Silicones.

Silicone resins can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit  $(\text{CH}_3)_3\text{SiO}_{1.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total

number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

Amino-substituted siloxanes useful herein include those represented by the following structure (II)



wherein R is CH<sub>3</sub> or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino-substituted siloxane fluids include those represented by the formula (III)

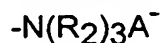
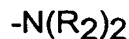
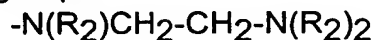


(III)

in which G is chosen from the group consisting of hydrogen, phenyl, OH, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sub>1</sub> is a

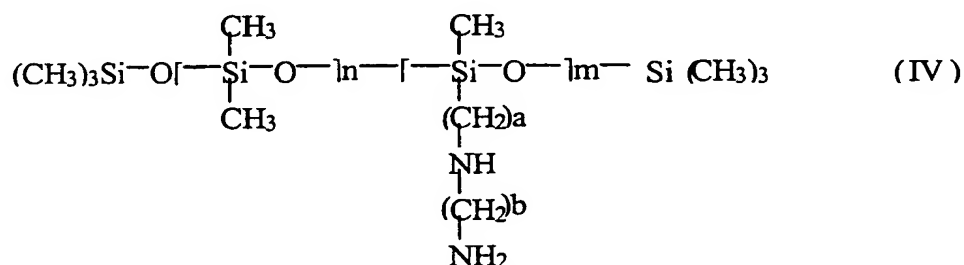


monovalent radical of formula  $C_qH_{2q}L$  in which  $q$  is an integer from 2 to 8 and  $L$  is chosen from the groups



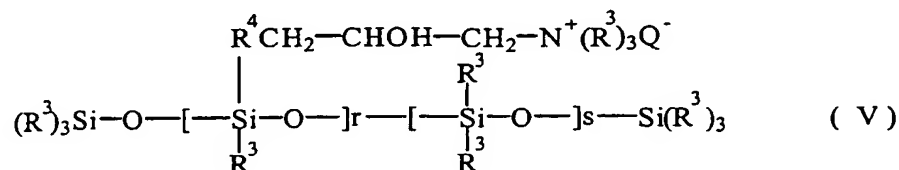
in which  $R_2$  is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and  $A^-$  denotes a halide ion.

An especially preferred amino-substituted siloxane corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



In this formula  $n$  and  $m$  are selected depending on the molecular weight of the compound desired.

Other amino-substituted siloxane which can be used are represented by the formula (V):



where  $R^3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $R^4$  denotes a hydrocarbon radical, preferably a  $C_1 - C_{18}$  alkylene radical or a  $C_1 - C_{18}$ , and more preferably  $C_1 - C_8$ , alkyleneoxy radical;  $Q^-$  is a halide ion, preferably

chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

5 In one preferred embodiment of the present invention, the silicone compound is contained in the hair conditioning composition in the form of a cationic silicone emulsion. The cationic silicone emulsion herein is a pre-dispersed stable emulsion comprising at least a cationic surfactant, a silicone compound, and water. The cationic surfactant useful herein is any known to the  
10 artisan, such as those selected from the species disclosed above under the title "Cationic Conditioning Agent".

The cationic silicone emulsion herein is also believed to minimize hair volume reduction, while not deteriorating conditioning benefits such as fly-away control. It is of particular significance that, in this preferred embodiment, the  
15 cationic surfactant is present in the silicone emulsion, and not just in the bulk of the composition. The cationic silicone emulsion herein also provides acceptable rheology profiles in conditioning compositions.

The cationic silicone emulsion typically contains, by weight of the cationic silicone emulsion, from about 1% to about 20%, preferably from about 2% to about 8%, of a cationic surfactant; and an emulsifiable amount of silicone  
20 compound. The silicone compound is preferably contained from about 0.1% to about 70%, more preferably from about 5% to about 60% by weight of the cationic silicone emulsion. The amount of silicone compound to the entire composition is preferably from about 0.1% to about 10% by weight.

25 The cationic silicone emulsion is included in the composition at a level by weight from about 0.1% to about 20%, more preferably from about 0.5% to about 5%.

The cationic silicone emulsion can be made by any convenient method known in the art.

30 For example, the cationic silicone emulsion may be made by mechanical emulsification by taking a polysiloxane polymer and emulsifying it in water in the presence of at least one emulsifying agent using mechanical means such as agitation, shaking and homogenization. The emulsifying agent can be the cationic surfactant comprised in the cationic silicone emulsion, or other suitable  
35 surfactant. Mechanical emulsification may require use of two or more

surfactants, and two or more mixing processes using different surfactants. Two or more types of silicone compounds, such as a highly viscous silicone compound and a low viscosity silicone compound, may be used. One particularly preferred process for obtaining the cationic silicone emulsion of the present invention via mechanical emulsification is through the process disclosed in EP Publication 460,683A, which is incorporated herein by reference in its entirety. In this reference, it is disclosed that the emulsion is prepared by combining the polysiloxane, water, and a primary nonionic surfactant having an HLB value of 15-19 to form a first mixture, adding to the first mixture a co-surfactant selected from the group consisting of nonionic, cationic and anionic surfactants having an HLB value of 1.8-15 to form a second mixture and mixing the second mixture at a temperature of about 40°C, until the particle size of the polysiloxane in the emulsion is less than about three hundred nanometers.

The cationic silicone emulsion herein may be made by emulsion polymerization. An emulsion polymerization process includes taking a polysiloxane monomer and/or oligomer and emulsifying it in water in the presence of a catalyst to form the polysiloxane polymer. It is understood that unreacted monomers and oligomers may remain in an emulsion polymerized silicone emulsion. One particularly preferred process for obtaining the cationic silicone emulsion of the present invention via emulsion polymerization is through the process disclosed in GB application 2,303,857, which is incorporated herein by reference in its entirety. This reference discloses a process for making stable cationic silicone oil-in-water emulsion comprising: 1) blending a mixture of silicones selected from the group consisting of cyclic silicone oligomers, mixed silicone hydrolyzates, silanol stopped oligomers, high molecular weight silicone polymers, and functionalized silicones with 2) water, and 3) an anionic surfactant; 4) heating the blend to a temperature ranging from about 75 to about 98°C for a period of time ranging from about 1 hours to about 5 hours; 5) cooling the heated blend to a temperature ranging from 0 to about 25°C for a period of time ranging from about 3 hours to about 24 hours; 6) adding a compatibilizing surfactant selected from the group consisting of nonionic surfactant having an HLB ratio greater than 9; and 7) adding a cationic surfactant.

The silicone compound in the cationic silicone emulsion has a particle size of less than about 50 microns, preferably from about 0.2 to about 2.5 microns, more preferably from about 0.2 to about 0.5 microns. The particle size of the

silicone compound is believed to affect the deposition of the silicone compound on the hair. The particle size of the silicone compound is determined based on the desired deposition and uniformity of distribution of the silicone compound.

### COMPOSITIONS

In one preferred embodiment of the present invention, the composition comprises:

- (a) from about 0.01% to about 2% of a hydrophobically modified cellulose ether;
- (b) from about 0.1% to about 10%, preferably from about 1% to about 7% of a high melting point fatty compound;
- (c) from about 0.1% to about 10%, preferably from about 0.25% to about 8%, more preferably from about 0.5% to about 3% of a cationic conditioning agent;
- (d) an aqueous carrier.

This composition can provide increase in bulk hair volume, softness, moisturized feel, and fly-away control. It can also provide satisfactory spreadability on the hair, and can be made by a convenient manufacturing method.

In another preferred embodiment of the present invention, the composition comprises:

- (a) from about 0.01% to about 2% of a hydrophobically modified cellulose ether;
- (b) from about 0.1% to about 10% of a high melting point fatty compound;
- (c) from about 0.55% to about 7%, preferably from about 1.2% to about 4.5% of a cationic conditioning agent, the cationic conditioning agent comprising an amidoamine and an acid; and
- (d) the aqueous carrier.

This composition may further contain a low melting point oil selected from the group consisting of pentaerythritol ester oils, trimethylol ester oils, poly  $\alpha$ -olefin oils, citrate ester oils, glyceryl ester oils, and mixtures thereof, which is preferably included in the composition at a level by weight of from about 0.1% to about 10%, more preferably from about 0.25% to about 6%.

This composition can provide provide the same benefits as those of the first embodiment, and further can provide the benefits such as slippery and slick feel on wet hair.

In another preferred embodiment of the present invention, the composition comprises:

A hair conditioning composition comprising:

- (a) from about 0.01% to about 2% of a hydrophobically modified cellulose ether;
- (b) from about 0.1% to about 5%, preferably from about 0.25% to about 2% of a high melting point fatty compound;
- (c) from about 0.1% to about 10%, preferably from about 0.25% to about 5% of a cationic conditioning agent;
- (d) an aqueous carrier;
- (e) from about 0.1% to about 10%, preferably from about 0.25% to about 6% of a low melting point oil, the low melting point oil being an unsaturated fatty alcohol; and
- (f) from about 0.1% to about 10%, preferably from about 0.25% to about 6% of a polyethylene glycol.

This composition can provides the same benefits as those of the first embodiment, and further can provide the benefits such as increase in bulk hair volume, softness, moisturized feel, and fly-away control on dry hair.

#### ADDITIONAL COMPONENTS

The composition of the present invention may include other additional components, which may be selected by the artisan according to the desired characteristics of the final product and which are suitable for rendering the composition more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such other additional components generally are used individually at levels of from about 0.001% to about 10%, preferably up to about 5% by weight of the composition.

A wide variety of other additional components can be formulated into the present compositions. These include: other conditioning agents such as hydrolysed collagen with tradename Pepten 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, a mixture of Polysorbate 60 and Cetearyl Alcohol with tradename Polawax NF available from Croda Chemicals, glycerylmonostearate available from Stepan Chemicals, hydroxyethyl cellulose available from Aqualon, hydrolysed keratin, proteins, plant extracts, and nutrients; hair-fixative polymers such as amphoteric fixative polymers, cationic

fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate, antidandruff agents such as zinc pyridinethione; and optical brighteners, for example polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof.

#### METHOD OF PREPARING COMPOSITION

The hair conditioning composition of the present invention may be made by any method of preparation known in the art.

In one embodiment, the hydrophobically modified cellulose ether is dispersed in water at room temperature to make a polymer solution, and is either heated up to above 70°C, or added to a water base preheated to above 70°C. Alternatively, the hydrophobically modified cellulose ether, which is typically obtained in the form of a powder, is directly added to the preheated water base. The cationic conditioning agent and the high melting point fatty compound are also added in the heated solution to form a gel matrix together with the hydrophobically modified cellulose ether. The mixture thus obtained is cooled down to below 60°C, and the remaining components are added with agitation, and further cooled down to about 30°C.

In a particularly preferred embodiment, the hair conditioning composition of the present invention is prepared by the following steps;

- (a) mixing the high melting point fatty compound, the cationic conditioning agent, and the aqueous carrier at a temperature of at least about 70°C;
- (b) cooling the mixture obtained in step (a) to below about 60°C;
- (c) adding the hydrophobically modified cellulose ether to the cooled mixture obtained in step (b); and
- (d) mixing until a homogeneous composition is obtained.

In step (a), the gel matrix is formed. The hydrophobically modified cellulose ether is added to this gel matrix, preferably after the gel matrix is cooled to a temperature of below about 60°C, still preferably about 40°C to 60°C in step (b). The hydrophobically modified cellulose ether can be added in the form of a powder, as typically obtained, or in the form of a partially or completely dissolved water solution in step (c). The obtained mixture is thoroughly mixed, as necessary using a triblender and/or mill, until homogeneous in step (d). When cationic polymers, polypropylene glycols or rheology modifiers are included in the composition, such components are added in either step (a) or (c). Any remaining components of the compositions are added in step (d). Heat sensitive components may be added after the mixture is cooled to room temperature.

Without being bound by theory, it is believed that, when the preferred embodiment method is used for preparing the present composition, the hydrophobically modified cellulose ether is mixed in the composition in a fully solubilized manner, thereby providing a stable composition in terms of rheology. Surprisingly, this stable composition may further provide an improved increase to bulk hair volume of the hair when applied to the hair.

### EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

The compositions of the present invention are suitable for rinse-off products and leave-on products, and are particularly useful for making products in the form of emulsion, cream, gel, spray or, mousse.

Examples 1 through 20 are hair conditioning compositions of the present invention which are particularly useful for rinse-off use.

#### Compositions of Examples 1 through 5

Components	Ex. 1	Ex. 2	Ex. 3	Ex 4	Ex. 5
Cetyl hydroxyethylcellulose-1 *1	0.2	0.25	0.25		0.1
Cetyl hydroxyethylcellulose-1 *2				0.25	
Cetyl Alcohol *3	4.5	1.5	1.5	1.5	4.5
Stearyl Alcohol *4	2.5	2.7	2.7	2.7	1.5

Behenyl Alcohol *5					1.0
Stearamidopropyl Dimethylamine *6	2.0	1.2	1.2	1.2	2.0
L-Glutamic Acid *7	0.64	0.384	0.384	0.384	0.64
Pentaerythritol Tetraisostearate *8	1.0				1.0
Cationic Silicone Emulsion-1 *9	1.05				
Cationic Silicone Emulsion-2 *10			0.69		
Silicone Blend *11		2.52		2.52	4.20
Preservatives	0.033	0.033	0.033	0.033	0.033
Benzyl alcohol	0.4	0.4	0.4	0.4	0.4
Perfume	0.6	0.6	0.6	0.6	0.6
Hydrolyzed collagen *12	0.01	0.01	0.01	0.01	0.01
Vitamin E *13	0.01	0.01	0.01	0.01	0.01
Panthenol *14	0.05	0.05	0.05	0.05	0.05
Panthenyl Ethyl Ether *15	0.05	0.05	0.05	0.05	0.05
Citric Acid *16	amount necessary to adjust pH 3-7				
Deionized Water	q.s. to 100%				

## Compositions of Examples 6 through 10

Components	Ex. 6	Ex. 7	Ex. 8	Ex 9	Ex. 10
Cetyl hydroxyethylcellulose-1 *1	0.25	0.25	0.1	0.25	0.25
Cetyl hydroxyethylcellulose-1 *2				0.25	
Cetyl Alcohol *3	0.96	0.96	1.2	0.96	0.7
Stearyl Alcohol *4	0.64	0.64	0.8	0.64	0.5
Behenyl Alcohol *5					0.20
Polawax NF *17	0.25	0.25	0.125	0.25	0.125
Stearamidopropyl Dimethylamine *6	1.0	1.0	1.0	1.0	0.75
Ditallow dimethyl ammonium chloride *18	0.75	0.75	0.75	0.75	0.5
Pentaerythritol Tetraisostearate *8			0.5		
Pentaerythritol Tetraoleate *19					0.5
Oleyl alcohol *20	0.25	0.25	0.10	0.25	0.25
PEG 2M *21	0.5	0.5	0.25	0.5	0.5
Cationic Silicone Emulsion-1 *9			0.8		
Cationic Silicone Emulsion-2 *10		1.05			3.0
Silicone Blend *11	4.2			4.2	
Glycerylmonostearate *22	0.25	0.25	0.25	0.25	0.25
Preservatives	0.04	0.04	0.04	0.04	0.04
Benzyl alcohol	0.4	0.4	0.4	0.4	0.4
Perfume	0.6	0.6	0.6	0.6	0.6



Acid EDTA	0.1	0.01	0.02	0.1	0.01
Hydrolyzed collagen *12	0.01	0.01	0.01	0.01	0.01
Vitamin E *13	0.01	0.025	0.01	0.01	0.01
Panthenol *14	0.05	0.2	0.1	0.05	0.05
Panthenyl Ethyl Ether *15	0.05	0.05	0.01	0.05	0.05
Citric Acid *16	amount necessary to adjust pH 3-7				
Deionized Water	q.s. to 100%				

Compositions of Examples 11 through 15

Components	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15
Cetyl hydroxyethylcellulose-1 *1	0.25	0.25	0.1		0.25
Cetyl hydroxyethylcellulose-1 *2				0.05	
Cetyl Alcohol *3	1.5	1.5	1.5	0.9	1.5
Stearyl Alcohol *4	2.7	2.7	2.7	0.64	2.7
Polawax NF *17				0.5	
Stearamidopropyl Dimethylamine *6	1.2	1.2	1.2	1.0	1.2
L-Glutamic Acid *7	0.384	0.384	0.384		0.384
Ditallow dimethyl ammonium chloride *18				0.75	
Oleyl alcohol *20				0.25	
PEG 2M *21				0.5	0.25
Silicone Blend *11	2.52	2.52	2.52	4.2	2.52
Glycerylmonostearate *22				0.25	
Preservatives	0.033	0.033	0.033	0.033	0.033
Benzyl alcohol	0.4	0.4	0.4	0.4	0.4
Perfume	0.6	0.6	0.6	0.6	0.6
Acid EDTA	0.1	0.1	0.1	0.1	0.1
Polyquaternium-24 *23	0.25				
Polyquaternium-24 *24			1.0		
Polypropylene Glycol *25		0.25	0.25		
Polyquaternium-4 *26	0.25				0.25
Polyquaternium-4 *27				0.25	
Hydroxyethyl Ethylcellulose *28				0.5	
Polygonum extract *29	0.1				
Biotin *30	0.1				
Citric Acid *16	amount necessary to adjust pH 3-7				
Deionized Water	q.s. to 100%				

Compositions of Examples 16 through 20

Components	Ex.16	Ex. 17	Ex. 18	Ex. 19	Ex.20
Cetyl hydroxyethylcellulose-1 *1	2.0	0.25	0.10	0.25	0.25
Cetyl hydroxyethylcellulose-1 *2				0.25	
Cetyl Alcohol *3	0.5	0.96	1.2	0.96	1.500
Stearyl Alcohol *4	0.9	0.64	0.8	0.64	2.70
Polawax NF *17		0.25	0.125	0.25	
Stearamidopropyl Dimethylamine *6	0.4	1.0	1.0	1.0	1.20
L-Glutamic Acid *7	0.13				
Ditallow dimethyl ammonium chloride *18		0.75	0.75	0.75	
Oleyl alcohol *20		0.25	0.1	0.25	
PEG 2M *21		0.5	0.25	0.50	
Silicone Blend *11	0.8	1.05	0.8	4.2	2.52
Glycerylmonostearate *22		0.25		0.25	
Preservatives	0.033	0.033	0.033	0.033	0.033
Benzyl alcohol	0.4	0.4	0.4	0.4	0.4
Perfume	0.6	0.6	0.6	0.6	0.6
Acid EDTA	0.1	0.1	0.1	0.1	0.1
Polyquaternium-24 *23					0.25
Polyquaternium-24 *24	0.1		1.0		
Polypropylene Glycol *25	0.1	0.2	0.1		0.25
Polyquaternium-4 *26					0.25
Polyquaternium-4 *27				0.5	
Hydroxyethyl Ethylcellulose *28	0.1	0.1	0.5	1.0	
Polygonum extract *29	0.1		0.1		
Biotin *30	0.1		0.1		
Citric Acid *16	amount necessary to adjust pH 3-7				
Deionized Water	q.s. to 100%				

Definitions of Components

- 5 \*1 Cetyl hydroxyethylcellulose-1: Polysurf 67 available from Aqualon.
- \*2 Cetyl hydroxyethylcellulose-2: NATROSOL PLUS 330CS available from Aqualon
- \*3 Cetyl Alcohol: Konol series available from Shin Nihon Rika.
- \*4 Stearyl Alcohol: Konol series available from Shin Nihon Rika.

- \*5 Behenyl Alcohol: 1-Docosanol (97%) available from Wako.
- \*6 Stearamidopropyl Dimethylamine: Amidoamine MPS available from Nikko.
- \*7 *l*-Glutamic Acid: *l*-Glutamic acid (cosmetic grade) available from Ajinomoto.
- \*8 Pentaerythritol Tetraisostearate: KAK PTI available from Kokyu alcohol.
- 5 \*9 Cationic Silicone Emulsion-1: PE2006 available from Dow Corning; mechanically emulsified emulsion containing 60% silicone compound and 3.0% cationic surfactant, wherein the silicone compound has a particle size of about 280 nm, and is made by using polydimethylsiloxane having about 900 repeating units and polydimethylsiloxane having about 100 repeating units, in a ratio of 27:73.
- 10 \*10 Cationic Silicone Emulsion-2: PE2016 available from Dow Corning; is mechanically emulsified emulsion containing 55% silicone compound and 3.0% cationic surfactant, wherein the silicone compound has a particle size of about 280 nm, and is made by using polydimethylsiloxane having about 900 repeating units and polydimethylsiloxane having about 100 repeating units, in a ratio of 27:73.
- 15 \*11 Silicone Blend: SE76 available from G.E.
- \*12 Hydrolyzed collagen: Peptin 2000 available from Hormel.
- \*13 Vitamin E: Emix-d available from Eisai.
- 20 \*14 Panthenol: available from Roche.
- \*15 Panthenyl Ethyl Ether: available from Roche.
- \*16 Citric Acid: Anhydrous Citric acid available from Haarman & Reimer.
- \*17 Polawax NF: Mixture of Polysorbate 60 and Cetearyl Alcohol available from Croda Chemicals.
- 25 \*18 Ditalow dimethyl ammonium chloride: available from Witco Chemicals.
- \*19 Pentaerythritol Tetraoleate: available from Shin NihonRika.
- \*20 Oleyl alcohol: available from New Japan Chemical.
- \*21 PEG-2M: Polyox available from Union Carbide.
- \*22 Glycerylmonostearate: available from Stepan Chemicals.
- 30 \*23 Polyquaternium-24: Quaterisoft Polymer LM-200 available from Amerchol
- \*24 Polyquaternium-24: BioCare Polymer HA-24 available from Amerchol
- \*25 Polypropylene Glycol: New Pol PP-2000 available from Sanyo Kasei
- \*26 Polyquaternium-4: Celquat L-200 available from National Starch Corp.
- \*27 Polyquaternium-4: Celquat H-100 available from National Starch Corp.
- 35 \*28 Hydroxyethyl Ethylcellulose: Elfacos CD 481 available from Akzo Nobel

\*29 Polygonum Extract: Polygonum multiflorum extract available from Lipo

\*30 Biotin: d-Biotin available from Roche

#### Method of Preparation

5 The compositions of Examples 1 through 20 as shown above can be prepared by any conventional method as follows: Cetyl hydroxyethylcellulose and, if present, polyethylene glycol are dispersed in water at room temperature to make a polymer solution, and heated up to above 70°C. Amidoamine and acid, or other cationic conditioning agents, and if present, ester oils are added in the solution with agitation. Then, the high melting point fatty compound, and if present, other low melting point oils and benzyl alcohol are also added in the solution with agitation. The mixture thus obtained is cooled down to below 60°C, and the remaining components such as silicone blend or cationic silicone emulsion are added with agitation, and further cooled down to about 30°C.

10 A triblender and/or mill can be used in each step, if necessary to disperse the materials.

15 In a particularly preferred embodiment, Examples 1 through 20 as shown above are prepared as follows: Amidoamine and acid, or other cationic conditioning agents, and if present, ester oils are added in the solution with agitation, and added to water base which was preheated to above 70°C. Then, the high melting point fatty compound, and if present, other low melting point oils and benzyl alcohol are also added in the solution with agitation. The Polyquaternium-24, Polyquaternium-4, Polypropylene glycol and hydroxyethyl ethylcellulose, if present, can be included at this point, or after the mixture is cooled. The mixture thus obtained is cooled down to between 40°C to 60°C, and the cetyl hydroxyethylcellulose and remaining components such as silicone blend or cationic silicone emulsion are added with agitation. The Polyquaternium-24, Polyquaternium-4, Polypropylene glycol and hydroxyethyl ethylcellulose can optionally be added at this stage. The finally obtained mixture is further cooled down to about 30°C.

20 A triblender and/or mill can be used in each step, if necessary to disperse the materials.

25 The embodiments disclosed and represented by the previous examples have many advantages. For example, they can provide increase in bulk hair volume, softness, moisturized feel, and fly-away control. They can also provide

satisfactory spreadability on the hair, and can be made by a convenient manufacturing method.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

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